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An ultrasmall Ru₂P nanoparticles-reduced graphene oxide hybrid: an efficient electrocatalyst for NH₃ synthesis under ambient conditions[†]

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Industrial NH₃ synthesis highly relies on the Haber–Bosch process which consumes a large amount of energy and emits a massive amount of CO₂. Electrochemical N₂ reduction is an eco-friendly and sustainable approach to realize NH₃ synthesis under ambient conditions, but its implementation requires efficient electrocatalysts for the N₂ reduction reaction. In this work, a hybrid of Ru₂P nanoparticles and reduced graphene oxide is proposed as an efficient electrocatalyst for artificial N₂-to-NH₃ fixation with excellent selectivity under ambient conditions. Electrochemical tests in 0.1 M HCl show that such a hybrid achieves a large NH₃ yield of 32.8 μ g h⁻¹ mg_{cat}⁻¹ and a high faradaic efficiency of 13.04% at -0.05 V vs. the reversible hydrogen electrode. Furthermore, it also exhibits remarkable electrochemical and structural stability. Theoretical calculations reveal that Ru₂P-rGO can efficiently catalyze NH₃ synthesis with a low energy barrier.

As one of the most produced chemicals, NH₃ is widely employed as a nitrogen source to produce fertilizers, medicaments, plastics, and so on.¹ Furthermore, with a considerable hydrogen content, high energy density and zero carbon emission, NH₃ is also considered an ideal candidate for energy storage and clean fuel.² Nowadays, industrial NH₃ synthesis is still predominantly performed by the Haber–Bosch process, which is conducted under harsh conditions with massive energy consumption and greenhouse gas emission.³ Therefore, a sustainable and economical approach is needed for artificial NH₃ synthesis under mild reaction conditions.

Electrochemical N2 reduction is an energy-saving and environmentally friendly approach which can replace the Haber-Bosch process for NH₃ synthesis under ambient conditions; however, efficient electrocatalysts for the N2 reduction reaction (NRR) are needed to break the inert N2 molecule.4-28 Ru performs efficiently in the traditional Haber-Bosch process.29 Ru is also theoretically predicted to be a good NRR electrocatalyst due to its appropriate overpotential and energy for N2 adsorption and activation, which are much lower than those of Pt and Pd.³⁰⁻³² A recent experimental study showed that Ru nanoparticles catalyze the NRR under ambient conditions with an NH₃ yield of 0.55 μ g h⁻¹ cm⁻² and a faradaic efficiency (FE) of 5.4%.33 Theoretical investigation further revealed that *N₂H_x species $(0 \le x \le 2)$ could accumulate on the surface of Ru due to the strong binding strength between them, resulting in a decreased performance toward the NRR.34 Obviously, to improve the NRR activity, the binding strength should be weakened. Bonding metal atoms with electronegative nonmetals is an effective way to weaken the binding strength through controlling the electron transfer between them.⁴ Our recent study verified that the NRR performance of a B catalyst is greatly improved by alloying with P due to further weakened N=N bonds.35 Hence, enhanced N2 reduction electrocatalysis is expected for the Ru catalyst after alloying with P, which however has not been explored before.

Herein, we report the development of an ultrasmall Ru₂P nanoparticles–reduced graphene oxide (Ru₂P–rGO) hybrid as an efficient NRR electrocatalyst for ambient N₂-to-NH₃ conversion with excellent selectivity. In 0.1 M HCl, this catalyst is capable of achieving a large NH₃ yield of 32.8 μ g h⁻¹ mg_{cat.}⁻¹ and a high FE of 13.04% at -0.05 V ν s. the reversible hydrogen electrode (RHE), superior to those of its Ru–rGO counterpart (6.4 μ g h⁻¹ mg_{cat.}⁻¹; 1.86%). Furthermore, it also exhibits remarkable electrochemical and structural stability. Density functional theory (DFT) calculations reveal that Ru₂P–rGO can efficiently catalyze NH₃ synthesis with a low energy barrier of 0.68 eV.

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The X-ray diffraction (XRD) pattern of Ru₂P-rGO is shown in Fig. 1a. The characteristic diffraction peaks at 30.5°, 38.1°, 40.6°, 42.2°, 47.1°, and 76.7° are indexed to the (111), (112), (211), (103), (020), and (403) planes of Ru₂P (JCPDS no. 65-2382). Transmission electron microscopy (TEM) analysis indicates that Ru₂P nanoparticles with ultrasmall diameters (2-4 nm) are uniformly anchored on the surface of rGO nanosheets (Fig. 1b). As shown in Fig. 1c, the high-resolution TEM (HRTEM) image depicts clear crystallographic fringes of Ru₂P-rGO with an average interplanar distance of 0.357 nm, which corresponds to the (112) lattice plane of Ru₂P. Furthermore, the selected area electron diffraction (SAED) pattern (Fig. 1d) shows three diffraction rings, which can be separately assigned to the (112), (103), and (403) planes of Ru₂P. Fig. 1e shows the scanning TEM (STEM) image and energy-dispersive X-ray (EDX) elemental mapping images of Ru₂P-rGO, which confirm the uniform distribution of Ru and P species on rGO nanosheet.

Fig. 2a shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of Ru₂P-rGO, which reveals the existence of Ru, P, C and O elements in the hybrid with Ru₂P about 38.69%. As shown in Fig. 2b, the peaks at 284.5 and 280.6 eV are assigned to the binding energies (BEs) of Ru $3d_{3/2}$ and Ru $3d_{5/2}$,^{36,37} while the peaks at 288.7, 285.8, and 284.9 eV are attributed to the O–C=O, C=O, and C=C bonds, respectively.³⁸ In the Ru 3p region (Fig. 2c), the peaks at 484.3 and 462.1 eV are assigned to the BEs of Ru $3p_{1/2}$ and Ru $3p_{3/2}$ peaks.³⁹ Note that the peaks at 486.9 and 464.3 eV can be ascribed to the oxidized RuP_x species.³⁹ In the P 2p region (Fig. 2d), the peaks located at 130.7 and 129.7 eV are



Fig. 1 (a) XRD pattern for Ru_2P-rGO . (b) TEM (inset: the particle size distribution of Ru_2P) and (c) HRTEM image of Ru_2P-rGO . (d) SAED pattern of Ru_2P-rGO . (e) STEM and EDX elemental mapping images of Ru_2P-rGO .



Fig. 2 (a) XPS survey spectrum of Ru_2P-rGO. XPS spectra of Ru_2P-rGO in the (b) C 1s and Ru 3d, (c) Ru 3p, and (d) P 2p regions.

consistent with the P $2p_{1/2}$ and P $2p_{3/2}$ peaks, respectively.⁴⁰ Additionally, the BE at 134.1 eV is ascribed to the P–O bond, which is formed by surface oxidation after exposure to air.³⁹ It is worth noting that the BE of Ru $3d_{5/2}$ (280.6 eV) exhibits a positive shift compared with that of metallic Ru (279.8 eV),⁴¹ while the BE of P $2p_{3/2}$ (129.7 eV) shows a negative shift compared with that of elemental P (130.2 eV).⁴² These shifts reveal that Ru possesses a partially positive charge, while P has a partially negative charge, implying that the electron density is transferred from Ru to P.³⁸

Ru₂P-rGO was loaded on carbon paper (Ru₂P-rGO/CP) with a loading of 0.1 mg cm^{-2} as the working electrode to evaluate the electrocatalytic NRR performance of this electrocatalyst in 0.1 M HCl. All potentials in the electrocatalytic NRR process were calibrated to the RHE scale. Chronoamperometry was performed at certain potentials ranging from 0.00 to -0.20 V for 2 h to obtain enough target product (NH₃) for quantitative evaluation of the catalytic activity of Ru₂P-rGO. As depicted in Fig. 3a, the current density increases with the increasing working potential. After electrolysis, NH₃ and the possible byproduct (N₂H₄) were determined by the indophenol blue⁴³ and Watt-Chrisp spectrophotometry methods,44 respectively. The corresponding calibration curves for NH3 and N2H4 are shown in Fig. S1 and S2,[†] respectively. Notably, the NH₄⁺ calibration solution was prepared in 0.1 M HCl. The UV-vis absorption spectra of the electrolytes dyed with the indophenol indicator after electrolysis for 2 h are displayed in Fig. 3b and employed to quantify the produced NH₃. The corresponding NH₃ yields and FEs are depicted in Fig. 3c. The largest NH₃ yield of 32.8 μ g h⁻¹ $\mathrm{mg_{cat.}}^{-1}$ and FE of 13.04% are achieved at -0.05 V under ambient conditions and are comparable to those of most noblemetal electrocatalysts under ambient conditions in aqueous electrolytes (Table S1[†]). Notably, when the applied potential is below -0.05 V, both the NH₃ yield and FE decrease, which is probably caused by the gradually enhanced competitive hydrogen evolution reaction.45

To further verify the superior catalytic performance of Ru_2P -rGO, a series of control experiments with catalysts such as Ru-



Fig. 3 (a) Chronoamperometry curves for Ru₂P-rGO/CP at different given potentials in 0.1 M HCl. (b) Corresponding UV-vis absorption spectra of the electrolytes stained with the indophenol indicator after NRR electrolysis at different potentials for 2 h. (c) NH₃ yields and FEs of Ru₂P-rGO/CP. (d) Amount of NH₃ produced using different electrodes at -0.05 V after 2 h of electrolysis under ambient conditions. (e) Recycling tests of Ru₂P-rGO/CP at -0.05 V. (f) Chronoamperometry curve for Ru₂P-rGO/CP at -0.05 V in a N₂-saturated electrolyte for 24 h.

rGO/CP, rGO/CP and blank CP were performed at -0.05 V for 2 h. As depicted in Fig. 3d, CP and rGO/CP exhibit low catalytic activity toward NH₃ synthesis. The better catalytic activity of Ru₂P-rGO/CP than of Ru-rGO/CP may be caused by the critical function of P in boosting the performance toward the NRR.³⁵ To verify the origin of the generated NH₃, NRR experiments using Ru₂P-rGO/CP under a N₂ atmosphere at open circuit and in Ar gas at -0.05 V were carried out. As shown in Fig. S3,[†] the weak UV-vis spectra indicate that the produced NH₃ stems from N₂ electroreduction. Notably, N₂H₄ was not detected in the final product (Fig. S4[†]), revealing that Ru₂P-rGO/CP possesses good selectivity for NH₃ synthesis by the NRR process.

As one of the important parameters to evaluate the performance of electrocatalysts, the stability should also be considered in the NRR process. Consecutive recycling tests were performed at -0.05 V in a N₂-saturated electrolyte 6 times and the corresponding results are shown in Fig. S5.† The well maintained NH₃ yields and FEs (Fig. 3e) reveal that Ru₂P-rGO/ CP is a stable electrocatalyst. In addition, the current density of Ru₂P-rGO/CP without obvious variation in 24 h of NRR electrolysis also suggests its excellent long-term stability as shown in Fig. 3f. Furthermore, the photographs of pH test papers for the HCl aqueous solution before and after 24 h of electrolysis are shown in Fig. S6,† which indicate that there is almost no change in pH in our experiment. In addition, we also analyzed the electrocatalytic NRR performance of Ru₂P-rGO/CP in 0.1 M Na_2SO_4 . The results indicate that the electrocatalytic NRR performance of Ru_2P -rGO in 0.1 M Na_2SO_4 is inferior to that in 0.1 M HCl (Fig. S7[†]).

The optimized geometries and Bader charge results before and after nitrogen molecule adsorption on Ru₂P-rGO are shown in Fig. 4a and b, respectively. P atoms have negative-mass electrons, which cover the positive charge of Ru, indicating net electron transfer from rGO to Ru₂P. Fig. 4b shows the detailed distribution of Bader charges after nitrogen adsorption. Clearly, the net charge on Ru₂P is slightly changed, due to donating 0.50 e^- to N₂. Interestingly, the two N atoms show slightly different charge values. To further understand the NRR catalytic site and mechanism of the Ru₂P-rGO, elementary steps associated with distal and alternating possible pathways for four potential N2-adsorption catalytic routes have been studied by DFT calculation (calculation details in the ESI[†]), including a single Ru site (1), two Ru sites (2), one Ru and one P site (3), and a single P site (4). The (3) and (4) possible catalytic sites are excluded after initial screening in this calculation, due to the fact that the P atom cannot adsorb a N2 molecule. Our calculations show that the dinitrogen molecule would indeed be well captured by the Ru atom, because the adsorption energies are negative on both the (1) and (2) possible catalytic sites. Moreover, the N-N distance increases from 1.10 Å in the free individual nitrogen molecule to 1.14 Å and 1.16 Å on the (1) and (2) possible catalytic sites, respectively, indicating that N2 is activated. The real challenge comes from the first hydrogenation step of N_2^* to N_2H^* , which requires a Gibbs free energy of about 1.30 and 0.68 eV on both possible pathways, respectively. The subsequent reduction steps of route 2 are the most exothermic, but the last desorption step (NH₃* to NH₃) requires energy input to complete the reaction (0.47 eV) (Fig. 4c and d). But all input energies are smaller than the first hydrogenation step energy,



Fig. 4 Optimized geometries and Bader charge results (a) before and (b) after N₂ adsorption on Ru₂P-rGO. Calculated energy profiles for the NRR catalyzed by Ru₂P-rGO: (c) distal and (d) alternating mechanisms.

indicating that the first reduction step is the potentialdetermining step (PDS) for both the distal and alternating mechanisms. However, the reduction steps of route 1 are endothermic reactions before the first NH₃-desorption, and all the free energies are lower than that in the first reduction step (Fig. S8†). Therefore, the dinitrogen molecule adsorbed on two Ru atoms (route 2) is the favorable reaction route for the NRR on Ru₂P–rGO, and the energy barrier of the NRR is equal to 0.68 eV for both mechanisms.

In conclusion, Ru₂P–rGO is experimentally and theoretically proved to be an efficient noble-metal electrocatalyst to realize artificial N₂-to-NH₃ conversion under ambient conditions. In 0.1 M HCl, Ru₂P–rGO achieves a large NH₃ yield of 32.8 μ g h⁻¹ mg_{cat.}⁻¹ and a high FE of 13.04% at -0.05 V. In addition, it also exhibits excellent selectivity toward NH₃ synthesis and long-term stability during the electrolysis test process. DFT calculations further reveal that Ru₂P–rGO can efficiently catalyze NH₃ synthesis with a low energy barrier of 0.68 eV and that the first hydrogenation step is the PDS. This investigation not only provides us with an efficient electrocatalyst toward NH₃ synthesis under ambient conditions, but also offers a path to design noble-metal-based phosphides for NRR applications.⁴⁶

Conflicts of interest

There are no conflicts to declare.

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